Synthesis of Composite Nanostructures for Synergistic Electrochemical Performance

Synopsis in candidature for the degree of

Doctor of Philosophy in Physics

Submitted By

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1. Introduction

A synergistic effect is the result of two or more processes interacting together to produce an effect that is greater than the cumulative effect that those processes produce when used individually. The concept is an important consideration chemical and physical sciences where one material can not satisfy entire expectations. Composites are made up with two or more than two materials of different structures, morphologies and optical properties for various applications [1]. It is generally accepted composite nanostructures are ideal for obtaining enhanced structural, morphological and shape-depended properties for better performance in chemiresistive, optoelectronic, and electrochemical devices [2]. They can effectively control electron, cavity, and exciton transmissions, and thus display unique properties such as Schottky diode phenomena, ohmic contact performance, and electrochemical properties [3]. With the advantages of the unique structures and morphological properties, solid-state photoelectronic detectors, biological/chemical sensors, and *p*–*n* heterojunction diodes have been successfully fabricated in the literature [4]. Additionally, composite nanostructures play a more important role in the construction of nanoscale devices as they possesses good thermal stability and low contact resistance [5].

1.1. Applications of composite nanostructures

1.1.1. Gas sensors

There is a need for simple, sensitive and stable electronic sensors suited for trace detection in a wide spectrum of applications ranging from lab-on-a-chip and *in-vivo* biosensors to environmental monitoring and warfare agent detection, as opposed to the often employed expensive, bulky and complicated instrumental methods. This need for inexpensive, low-power devices is fueling the exponential growth of research in this area [6]. There are certain gases which can be toxic for humans, and can cause big explosions. Accordingly, there is a need of gas sensors with the intention of continuous and effective detection of these gases to evade predominantly the above said dangers. An ideal gas sensor should possess the following sensing properties [7]:

- High Sensitivity to certain gases
- Reversibility
- Faster response time and good recovery time.
- High Selectivity
- Long term Stability
- Simple principle of operation
- Easy to handle.

- Simple fabrication techniques.
- Temperature insensitive.

It is expected that due to composite nanostructures sensor material will show either better performance for one and two gases or exhibits better performance for the one and same gas as synergistic effect in sensor studies.

1.1.2. Electrochemical Supercapacitors

Development of sustainable energy resource is essential for living species not only for completing basic needs but also for availing future needs. The growing energy crisis in recent decades due to the rising cost of fossil fuels, depletion of fossil fuels is serious and has adverse impact on issues like environmental pollution and global warming [8]. The electrochemical storage devices can be the solution for all these obstacles. The most promising electrical energy storage devices are conventional capacitors, electrochemical capacitors (ECs), batteries, and fuel cells etc., where chemical energy is converted into electrical energy. ECs are also known as supercapacitors which act as a bridging function for the energy/power between batteries and fuel cells and have high energy-power storage capacity [9]. There are two types of supercapacitors, symmetric supercapacitor and asymmetric supercapacitor. Symmetric supercapacitor includes Electrostatic double-layer capacitor or pseudocapacitor. While asymmetric super capacitor possesses hybrid super capacitor. Symmetric super capacitor uses electrode with same characteristics while asymmetric super capacitor uses electrodes with different characteristics one exhibit mostly electrostatic capacitance and the other mostly electrochemical capacitance. There are two major mechanisms found in ECs: (a) Electrochemical double-layer capacitors (EDLCs) where diffusion mechanism is dominant and reaction takes place as electrode/electrolyte interface, and (b) Faradaic supercapacitors (FS) or pseudocapacitors where redox reactions are effective due to availability of various redox states. The remarkable performance of pseudocapacitor materials compared to that of the EDLC materials in supercapacitors open up new research possibilities, particularly in transition metal oxides like nickel oxide [10]. EDLCs offer good cyclic stability, good power performance while in the case of pseudo capacitance it offers greater specific capacitance. In the case of hybrid system, it offers a combination of both, that is by combining the energy source of battery-like electrode, with a power source of capacitor like electrode in the same cell [10]. With a correct electrode combination, it is possible to increase the cell voltage, which in turn leads to an improvement in energy and power densities. Several alternative electrode materials are being investigated, including metal oxides, metal hydroxides, metal sulfides, conducting polymers, and carbonaceous materials [11]. Metal oxides such as RuO_2,

Co_3O_4, MnO_2, and NiO are the most promising materials for pseudocapacitor because of their highspecific capacitance. The pseudocapacitor properties of RuO_2 have attracted a great deal of attention because of their high electrochemical stability, wide potential window, and high specific capacitance.However, the high cost, limited surface area and toxicity of RuO_2 and drop the active sites during the heat treatment temperatures in the case of $RuO_2.xH_2O$ are inhibiting proton intercalation that leading to a decrease in specific capacitance that made the main reason to limits its commercial application [12]. Hence, NiO is a promising alternative transition metal because it is abundant, cheap and good electrochemical stability, and is a *p*-type semiconductor, with a wide band-gap of 3.6–4.0 eV [13].

Using one electrode material in electrochemical supercapacitors in three electrodes system potential window will be either negative or positive, under synergistic effect it is expected that the composite nanostructures will demonstrate enhanced potential window either in same side or in different side.

1.1.3.Electrocatalysis

Due to escalating demand of the clean and renewable energy caused by backdrop calamity and environmental pollution, the development of promising energy storage and conversion devices, i.e., catalysts, became obligatory. Hydrogen is a promising option for clean energy, which can be produced by splitting water either in an electrocatalyzer or by photocatalysis. Electrochemical water splitting involves the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Both reactions require a proper catalyst to boost the reaction kinetics. So far, precious metals (Pt, Ru, and Pd) and noble metal oxides (IrO_2) showed the best performance toward both OER and HER. However, owing to the high cost and scarcity, they are obstructed. Researchers have made several efforts to develop nonprecious metal-based catalysts for water splitting such as from sulfides, selenides, oxides, etc. [14]. Among the known catalysts, Heterojunction-based composite nanostructured electrode materials have demonstrated an excellent chemical and mechanical stability and porosity, high surface area, fine controlled pore coordination, i.e., pore-size distribution and connectivity, good conductivity, low cost, and stability. However, owing to the sluggish reaction kinetics, there is still need to prepare the electrocatalysts with enhanced performance with lower overpotential and minute Tafel slope [15].

In electrocatalysts studies on forming composite nanostructures either both activities *i.e.*, OER and HER or one activity with minimum overpotential will be obtained.

1.2. Methodology

1. Synthesis of metal oxides and their composites using chemical methods.
2. The required nanomaterials will be prepared using various synthesis methods like, Chemical bath deposition (CBD), Successive ionic layer adsorption and reaction (SILAR), Hydrothermal synthesis, Spray pyrolysis. Along with these methods other synthesis methods will be adopted if necessary.
3. Composite electrodes will be prepared by dipping samples in table top sugar baths of different concentrations
4. These electrodes will be annealed for forming composite nanostructures.

1.3. Characterization details:

A concise account of the instruments and techniques used for acknowledgement of structural, morphological, electrical and gas sensing properties of the sensor sample, are discussed in this section.

1.3.1. Structural studies

X-ray diffraction (XRD) technique is a one of the influential, renowned and most appropriate techniques for structural revelation of materials prepared in the form of films or powders.

1.3.2. Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to observe vibration, rotational, and other low-frequency modes in a system.

1.3.3. Fourier Transform Infrared Spectroscopy

FT-IR spectroscopy is a tool for investigation of the various chemical groups present in the sample material.

1.3.4. Morphological analysis

Field-emission Scanning Electron Microscopy will be used for investigating the surface morphology of the as-prepared composite electrodes.

1.3.5. High Resolution Transmission Electron Microscopy

HR-TEM is one of most powerful techniques used in the characterization of Nanocomposites. It has capacity to inspect the constitutional characteristics of Nanocomposites such as grain shape and size, crystallinity and chemical variations at a nanometer scale resolution.

1.3.6. Gas Sensor setup

The change in resistance of the sensor, due to the presence of target gas, can be recorded by using Computer assisted 6-digit Keithley 6514 System electrometer. Keithley electrometer

was coupled to the computer via RS232 interface to record the change in resistance with respect to time.

1.3.7. Electrochemical workstation

The as-prepared heterojunction composite nanostructures are used to prepared electrodes for supercapacitor and electrocatalysis applications. The IVIUM electrochemical workstation is used to measure Cyclic Voltammetry (CV), Galvanostatic charge-discharge (GCD) and Electrochemical impedance spectroscopy (EIS) for materials electrochemical characterizations. Also, Mott-Schottky measurements will be carried out for confirmation of type of conductivity of the composite nanostructures.

1.4. Objectives

This thesis aims at achieving the following objectives:

1. Synthesis and characterizations of composite nanostructures of metal oxides and carbonaceous materials.
2. To study the chemiresistive gas sensor performance of these composite nanostructured sensors.
3. To study the electrochemical performance of these composite nanostructured electrodes in there electrode systems.
4. Utilization of these composite nanostructured electrodes in electrocatalysis applications.

1.5. Plausible outcomes

- Synthesis of composite nanostructures with their physical and chemical properties
- Fabrication of composite nanostructure-based electrochemical supercapacitor devices with high energy and power density as well as moderate stability.
- Fabrication of composites as a potential electrocatalystfor OER and HER activities.
- Writing and Publishing research articles, reviews and patents in different international journals.

1.6. References:

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